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(54) Title of Invention: Nubuck-like Leathery Sheet and Its Manufacturing Method

(57) Abstract:

[Purpose] To provide a nubuck-like leathery sheet which can be manufactured at manufacturing costs as much as those in the wet process and which has a high quality equivalent to the one obtainable by the wet process, and its manufacturing method

[Constitution] This nubuck-like leathery sheet is obtained by buffing the convex parts of a skin layer having matte concavo-convex patterns made of polyether-based polyurethane resin.

[Claims]

[Claim 1] A nubuck-like leathery sheet characterized in that a skin layer made of polyether-based polyurethane resin having matte concavo-convex patterns is formed on a substrate, and the convex parts of said skin layer is buffed off.

[Claim 2] The nubuck-like leathery sheet according to claim 1 in which the difference in the level of the convex and concave parts of said skin layer is at least 5  $\mu\text{m}$ .

[Claim 3] The nubuck-like leathery sheet according to claim 1 in which said skin layer is bonded to the substrate by a polyurethane resin adhesive.

[Claim 4] A manufacturing method of a nubuck-like leathery sheet characterized in that a skin layer made of polyether-based polyurethane resin having matte concavo-convex patterns is bonded to a substrate, and the convex parts of said skin

layer is buffed off.

[Claim 5] The manufacturing method of a nubuck-like leathery sheet according to claim 4 in which said polyether-based polyurethane resin contains an amount of 50 wt% or more polyether and its 100% modulus is 150 kg/cm<sup>2</sup> or less.

[Claim 6] The manufacturing method of a nubuck-like leathery sheet according to claim 4 in which a skin layer formed on a matte release paper by applying a polyether-based polyurethane resin is bonded to the substrate.

#### [Detailed Description of the Invention]

[0001]

[Industrial Application] The present invention relates to a nubuck-like leathery sheet with appearance and texture similar to the natural leather nubuck (suede), and a manufacturing method for the same.

[0002]

[Description of the Prior Art] Nubuck-like leathery sheets have been manufactured and put in actual use such that naps of ultrafine fibers are formed on the skin layer and the naps are then cut to short by buffing using a sand-paper etc., or a polyurethane resin is applied onto the substrate and the skin layer on the surface of which micro-porous coating was previously formed by the wet process is removed by buffing. Generally speaking, the nubuck-like sheets mean, in many cases, those made by the latter method. However, the said method takes a long time in the production process and the manufacturing facilities to be used are rather limited and thus, price of the product will become higher. Therefore, its sales volume cannot be easily increased in spite of its high quality.

On the other hand, products manufactured by the so-called dry process (not forming micro-porous coating), wherein the skin layer and bonding layer are applied onto a release paper to paste them with the release paper, do not need the manufacturing facility for the wet process and thus, the products are advantageous in terms of manufacturing costs. However, the final product shows neither surface touch nor appearance equivalent to those made by the wet process and thus, they have problems in terms of quality.

[0003]

[Problem(s) to be Solved by the Invention] The present invention provides a nubuck-like leathery sheet boasting of good quality equivalent to the one achievable by the wet system which can be manufactured at manufacturing costs equivalent to those of the dry process by manufacturing facilities being not limited to the

manufacturing facility on the basis of wet process, and a manufacturing method for the same.

[0004]

[Means for Solving the Problem] According to the present invention, a nubuck-like leathery sheet is provided which is characterized in that a skin layer made of polyether-based polyurethane resin having matte concavo-convex patterns is formed on a substrate, and the convex parts of said skin layer is buffed off. In addition, according to the present invention, a production method of a nubuck-like leathery sheet is also provided which is characterized in that a skin layer made of polyether-based polyurethane resin having matte concavo-convex patterns is bonded to a substrate, and the convex parts of said skin layer is buffed off.

[0005]

[Effect] By buffing the surface of the convex parts of the matte concavo-convex patterns of the skin layer, the luster of the concave and convex parts comes closer so that the whole skin layer is getting matte to increase its hyper-chromic effect. Moreover, it is possible to produce a nubuck-like leathery sheet which is rich in elasticity, wetness and surface strength and has a touch full of soft slimness.

[0006]

[Preferred Embodiments] The present invention will be explained in detail by the following preferred embodiments. The nubuck-like leathery sheet of the present invention has a structure produced by bonding a skin layer onto a substrate, in which matte concavo-convex patterns are formed on the surface of the skin layer and only the convex parts of said patterns are buffed off. Examples of the substrate used in the present invention include woven and/or nonwoven-fabrics made of natural or synthetic fibers, which have been used for manufacturing leathery sheets, but not particularly limited to them.

[0007] In addition, the skin layer is formed by coating without formation of any micro-porous coating and the coating of a polyether-based polyurethane resin is particularly suitable as its material in terms of the forming property of matte concavo-convex patterns on the surface, the elasticity and qualities of the final product, such as wetness, sliminess etc. To provide such qualities, polyurethane resins having a 100 %-modulus of not more than 150 kg/cm<sup>2</sup> are preferred. Polyether/ester-based or polyether/carbonate-based polyurethane resins are preferred as the polyether-based polyurethane resin, and more preferable are those containing at least an amount of 50 wt% or more polyether in polyurethane. The thickness of the skin layer is usually 20 - 40  $\mu$ m. For the purpose of coloring, a

variety of pigments and other compounding agents can be added to the polyether-based polyurethane resin.

[0008] Methods for forming matte concavo-convex patterns on the skin layer are not particularly limited. Preferred methods are: using a release paper having matte concavo-convex patterns on its surface and applying a solution of polyether-based polyurethane resin onto the release paper by coating and the like; or forming a coating of said polyurethane resin on the release paper by producing said polyurethane resin on the release paper, followed by peeling off the release paper to transcribe the matte patterns onto the coating surface. The leathery sheet of the present invention, in which only the convex parts of the matte concavo-convex patterns on the skin layer are buffed off, has preferably a difference of at least 5  $\mu\text{m}$  between the top and bottom levels (i.e. the depth of grain), so that said convex parts only may be buffed off.

[0009] The skin layer thus obtained is bonded to the substrate. Adhesives to be used are not particularly limited, as long as they can firmly bond the two layers without degrading the quality of product, and preferable is a polyurethane-based adhesive. The total thickness of the skin layer and the adhesive layer required is to be 40  $\mu\text{m}$  or more in the light of the texture, strength etc. of the leathery sheet. Thicknesses exceeding 80  $\mu\text{m}$  are not preferable, because its texture will become worse in that case.

[0010] At last, only the skin layer on the convex parts of the concavo-convex patterns formed on the skin layer is buffed off. The buffing is usually performed by using a sand-paper or the like, but is not limited thereto. By buffing only the surface of the convex parts, the luster of the concave and convex parts comes closer so that the whole skin layer is getting matte. Fig. 1 shows a schematic view of the leathery sheet of the present invention.

[0011]

[Working Examples] The present invention will be further illustrated by the following Working and Comparative examples. Unless otherwise specified, "part(s)" and "%" in the following Working and Comparative examples are on the basis of weight.

[0012] Working example 1

To 100 parts of a solution of polyether-based polyurethane resin [solid content at 30%, methylethyl ketone (MEK)/dimethyl formamide (DMF) = 1/1] having a 100%-modulus of 20  $\text{kg}/\text{cm}^2$ , were added 20 parts of a black colorant (carbon black content at 15%) and each 25 parts of DMF and MEK (diluting solvents), and the

resulting solution was applied to a release paper (Ultra-suede manufactured by Asahi Release Co., Ltd.) at a ratio of approx. 150 g/m<sup>2</sup> (wet basis) and dried to produce a coating 30 μm thick for forming the surface skin. A mixed solution (approx. 120 g) as an adhesive was then applied thereto, which was prepared by adding 10 parts of a crosslinker to 100 parts of a polyether-based two-component polyurethane [solid content at 40%, MEK/toluene/DMF] to paste the coating with the substrate. After completion of cross-linking, the release paper was peeled off (the total coating thickness of polyurethane on the skin and adhesive layers applied onto the substrate after drying was approx. 60 μm). The convex parts on the skin layer of the leathery sheet thus obtained were buffed off with a #240 sand-paper to complete the final product. The resultant product had a matte appearance with intense black content, in addition to its surface touch full of soft slimness.

[0013] Working example 2

In the same manner as the above Working example 1, except for using a solution of polyether/ester (6/4)-based polyurethane resin (solid content at 30%, MEK/DMF = 1/1) having a 100%-modulus of 50 kg/cm<sup>2</sup>, a nubuck-like leathery sheet was obtained.

[0014] Working example 3

In the same manner as the above Working example 1, except for using a solution of polyether-based polyurethane resin (solid content at 30%, MEK/DMF = 1/1) having a 100%-modulus of 90 kg/cm<sup>2</sup>, a nubuck-like leathery sheet was prepared.

[0015] Working example 4

In the same manner as the above Working example 1, except for using a solution of polyether/ester (7/3)-based polyurethane resin (solid content at 30%, MEK/DMF = 1/1) having a 100%-modulus of 50 kg/cm<sup>2</sup> and a release paper EV130TPD (R-8) manufactured by Lintec Corp., a nubuck-like leathery sheet was obtained.

[0016] Comparative example 1

In the same manner as the above Working example 1, except for using a solution of polyester-based polyurethane resin (solid content at 30%, MEK/DMF = 1/1) having a 100%-modulus of 90 kg/cm<sup>2</sup> and a release paper EV130TPD (R-8) manufactured by Lintec Corp., a nubuck-like leathery sheet was obtained.

[0017] Comparative example 2

To 100 parts of a solution of polyester-based polyurethane resin (a DMF solution with a 30%-solid content) having a 100%-modulus of 30 kg/cm<sup>2</sup>, were added 20 parts of a colorant (carbon black content at 15%), an appropriate volume of a coating auxiliary agent and 40 parts of DMF, and the mixed solution was then applied onto

the substrate at an amount of approx. 1000 g/m<sup>2</sup>, and the substrate was immersed in water for approx. 15 minutes to remove DMF, so that the polyurethane was solidified. In addition, the resultant substance was washed with hot water of approx. 50 °C for 1 hour to completely remove DMF and further dehydrated/dried to obtain a micro-porous polyurethane coating. The whole surface was buffed off with a sand-paper to produce a nubuck-like leathery sheet.

[0018]

[Evaluation Results] The nubuck-like leathery sheets obtained in the Working and Comparative examples as mentioned above were evaluated for their textures, black contents and manufacturing costs, according to the following evaluation criteria. The results are shown in Table 1.

#### Evaluation criteria

##### (1) Texture

⊙: Remarkably soft and slimy touch, and highly available for practical use

○: Soft and slightly slimy touch, and available for practical use

△: Not soft touch, and not available for practical use

X: Rough touch, and totally impracticable

##### (2) Black content

⊙: Matte and intensely black, and highly available for practical use

○: Matte and adequately black, and available for practical use

△: Matte and inadequately black, and not available for practical use

X: Inadequately matte and black, and totally impracticable

##### (3) Manufacturing costs

⊙: This sign denotes those obtained by the dry process in Comparative example 1.

○: This sign denotes a practicable one ranked between those obtained in Comparative examples 1 and 2.

X: This sign denotes those obtained by the wet process in Comparative example 2.

[0019]

[Table 1]

	Texture	Black content	Costs
Working example 1	⊙	⊙	○
Working example 2	○	⊙	○
Working example 3	○-△	⊙	○
Working example 4	○	○	○
Comparative example 1	△	X	⊙

Comparative example 2	◎	◎	X
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[0020]

[Effect of the Invention] The nubuck-like leathery sheet of the present invention is useful as a material for a variety of clothing items, because it has a great elasticity, wet and slimy texture, matte appearance, intense hyper-chromic effect, and excellent surface strength. In addition, this nubuck-like leathery sheet can be easily and inexpensively produced by buffing the convex parts only of matte concavo-convex patterns on the skin layer.

[Brief Description of the Drawings]

[Fig. 1] A production example for the nubuck-like leathery sheet of the present invention is shown in Fig. 1.

[Fig. 1]

